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(54) Title: FERROMAGNET

(57) **Abstract:** Described is a ferromagnetic material comprising a substituted conjugated polymer which comprises a conjugated polymer which is substituted with an organic electron acceptor. The material is preferably ferromagnetic at room temperature (290K) and, most preferably, is ferromagnetic at temperatures above room temperature. In a preferred embodiment, the conjugated polymer is polyaniline and the electron acceptor is tetracyanoquinodimethane (TCNQ). Also described is a method for producing the substituted conjugated polymer and uses of the material.

"Ferromagnet"

This invention relates to a room temperature ferromagnetic non-metallic material and, in particular, to a room temperature ferromagnetic polymer.

In recent years there has been a large interest in the formation of new magnetic materials from non-metallic molecules. So far polymers have failed to make an impact in this area, mainly because of the difficulties posed in the production of highly ordered or even crystalline polymers. Such structural order is required to observe magnetic effects.

In particular, there has been little progress in the formation of non-metallic ferromagnetic materials. Ferromagnetic materials have many applications e.g., for electromagnets, transformers, magnetic tape recording, magnetic shielding, magneto-optical data storage and magnetic transistors. Almost all known

ferromagnetic materials are metallic in nature. As such their production may attract processing difficulties, for example, due to the heaviness of the material, and they may be expensive to produce.

A problem associated with the production of a non-metallic ferromagnetic material is that of synthesising molecules which have a high enough density of localised spins which are physically close enough in space to yield a high enough exchange interaction for the material to exhibit ferromagnetism. The molecules in a ferromagnetic material need to be positioned so that the weak exchange interactions between each spin give rise to ferromagnetic ordering. This is difficult to achieve and, in almost all cases, it is found that the exchange interaction is so weak that a ferromagnetic phase is only observed at low temperatures such as 2-4 K. Difficulties can arise in the preparation of non-metallic ferromagnetic materials, for example, when radicals are generated by oxidation. In these cases it is difficult to maintain a high packing density and degree of order, whilst permitting access of the oxidising agents into the structure to form the radicals.

It follows that another problem associated with the production of non-metallic ferromagnetic materials is that of producing a material which is ferromagnetic at room temperature (i.e. 290 K) or higher, i.e. has a Curie temperature (T_c) of greater than or equal to room temperature. Clearly this has

implications for the end use of the material. To date, there has been only one report of room temperature ferromagnetic non-metallic material (Markarova T. L. et al, Magnetic Carbon, Nature, 413, 716-718 (2001) reported a weakly ferromagnetic phase in C_{60} at room temperature). However, the results of this report are clearly non-reproducible.

It is therefore an aim to provide a ferromagnetic non-metallic material. In particular, it is an aim to provide a non-metallic material that is ferromagnetic at room temperature.

The present invention provides a substituted conjugated polymer comprising a conjugated polymer which is substituted with an organic electron acceptor.

In particular the present invention provides a ferromagnetic material comprising a conjugated polymer which is substituted with an organic electron acceptor. The material is ferromagnetic at temperatures above 200K, preferably ferromagnetic at temperatures above 250K, more preferably ferromagnetic at room temperature (290K) and, most preferably, is ferromagnetic at temperatures above room temperature. In a particularly preferred embodiment, the material of the present invention is ferromagnetic up to 400K, more preferably up to 500K. The material has a mass magnetisation at room temperature of at least 0.003 $JT^{-1}Kg^{-1}$. More preferably, it has a mass magnetisation at room

temperature of between 0.003 and 10 $JT^{-1}Kg^{-1}$, more preferably between 0.003 and 20 $JT^{-1}Kg^{-1}$, most preferably between 0.003 and 30 $JT^{-1}Kg^{-1}$.

By conjugated polymer is meant that the polymer comprises alternating single and double bonds between carbon atoms so that a π electron system is formed along the polymer chain. Preferably the conjugated polymer comprises aromatic groups. These aromatic groups may be heterocyclic aromatic groups and in a preferred embodiment the heterocyclic aromatic groups contain a nitrogen atom in the ring structure. Examples of suitable conjugated polymers are polyaniline, polypyridine, polypyrrole, polyparaphenylene, polyphenylene-vinylene (PPV), polythiophene or polyfluorene. The conjugated polymer can be a polymer obtainable by polymerising substituted monomers of aniline, pyridine, pyrrole, phenylene, phenylene-vinylene, thiophene or fluorene. For example, poly(2-methoxy,5-(2'-ethyl-hexyloxy)-p-phenylenevinylene (MEH-PPV) is a suitable conjugated polymer obtainable by polymerising substituted phenylene-vinylene monomers.

In a preferred embodiment the conjugated polymer is polyaniline or is a polymer obtained from substituted aniline monomers. The term polyaniline includes all different forms of polyaniline (leuco-emeraldine base, emeraldine base and pernigraniline). Emeraldine base polyaniline is particularly preferred. The emeraldine base

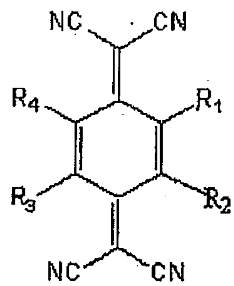
polyaniline is prepared by the method outlined by A.P. Monkman et al in Low Temperature Synthesis of High Molecular weight Polyaniline, Polymer, 37, 3411-3417 (1996).

The conjugated polymer preferably has a number average molecular weight of greater than 4000 and more preferably greater than 19000 Dalton. Typically the number average molecular weight is in the range of 4000 to 250 000 Dalton.

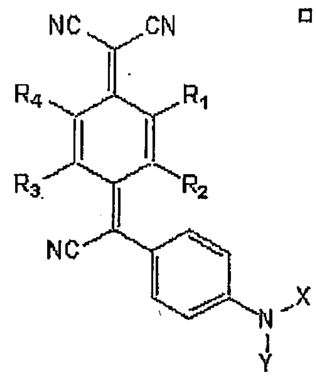
The organic electron acceptor forms a charge transfer complex with the conjugated polymer. Preferably the organic electron acceptor readily forms radicals.

The organic electron acceptor may be chosen from: tetracyanoquinodimethane (TCNQ); tetracyanonapthoquinodimethane (TNAP); tetracyanoethylene (TCNE); dichlorodicyanobenzoquinone (DDQ); TCNQ derivatives; or other such electron acceptors.

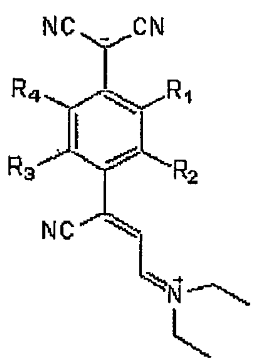
The family of TCNQ derivatives includes, but is not limited to, the following:



Formula I



Formula II



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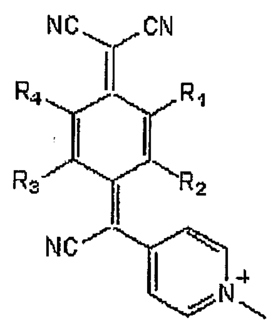
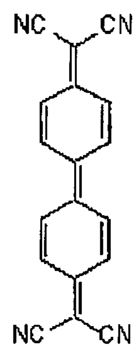


Formula IV

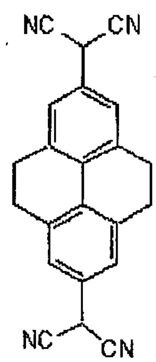
where
$R_1 = R_2 = R_3 = R_4$ = F, Me, Ph or NCHCHN; or
$R_2 = R_4$ = H and $R_1 = R_3$ = I, Br, OMe, CN, $PhCH_2$, a C_1-C_8 alkyl group (preferably hexyl, Me, Et or iPr); or
$R_2 = R_4$ = H and R_1 = OMe and R_3 = OEt, OiPr, OiButyl, OiPentyl; or

$R_2 = R_4 = H$ and $R_1 = OEt$ and $R_3 = SMe$; or
$R_2 = R_4 = H$ and $R_3 = Me$ and $R_1 = I$, Br or Cl; or
$R_1 = R_2 = OCH_2CH_2O$ and $R_3 = OMe$ and $R_4=H$; or
$R_2 = R_4 = H$ and $R_3 = Br$ and $R_1 = OCH_2CH_2OH$; or
$R_2 = R_3 = R_4 = H$ and $R_1 = Me$, Et, OMe, CO_2Me,; and
$X = Y = C_1-C_8$ alkyl group or CH_2CH_2OH; or $X = C_1-C_8$ alkyl group and $Y = CH_2CH_2OH$

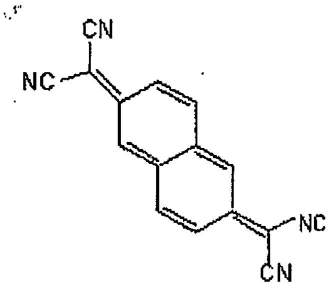
The following structures are also included within TCNQ derivatives:



Formula V



Formula VI



Formula VII

In preferred embodiments of the invention, the organic electron acceptor is preferably tetracyanoquinonedimethane (TCNQ). This is a stable radical forming molecule which readily forms charge transfer complexes with electron donors such as nitrogen atoms on a heterocyclic conjugated polymer having nitrogen in its ring structure.

It is believed that the mass magnetisation of the material depends on the degree of substitution of the polymer backbone with the organic electron acceptors. Preferably the degree of substitution is such that the ferromagnetic material has a mass magnetisation at room temperature of at least 0.003 $JT^{-1}Kg^{-1}$.

The present invention also provides a method for producing a ferromagnetic polymer which method comprises reacting a conjugated polymer with an organic electron acceptor.

In a preferred embodiment the method comprises the following steps:

a) dissolving the conjugated polymer in an appropriate solvent,

b) adding the organic electron acceptor to the solution and refluxing the resultant solution for at least 24 hours,

c) cooling and filtering the refluxed solution from step b and collecting and evaporating the filtrate to form a solid polymer,

d) drying the polymer from step c, and allowing the polymer to reach a steady ferromagnetic state.

Typically, the conjugated polymer is dissolved in an appropriate solvent, e.g. n-methyl-2-pyrollidinone

(NMP). The organic electron acceptor is added to the solution and the mixture is refluxed for at least 24 hours. Typically the molar ratio of polymer and organic electron acceptor in the mixture is 1:2. The solution is then cooled and filtered. The filtrate is collected and evaporated to form a solid polymer. This polymer is then dried under vacuum at 80°C. The polymer is then left until it reaches a steady ferromagnetic state. Typically this will take any time up to 4 weeks. Preferably the polymer remains in a vacuum or in an inert atmosphere during this step.

In a particularly preferred embodiment the conjugated polymer is the emeraldine base form of polyaniline and the organic electron acceptor is TCNQ. The resultant substituted conjugated polymer is polyaniline tricyanoquinonedimethane (PANiCNQ). Not wishing to be bound by any theory, it is believed that PANiCNQ contains stable radicals which are generated by charge transfer from the TCNQ to the amine sites on the conjugated polymer and by protonation of the imine sites on the conjugated polymer. π-stacking of neighbouring chains may occur and may result in interchain spacing of approximately 4 Angstrom or less. This gives rise to exchange interactions between neighbouring chains and hence a three dimensional ferromagnetic exchange mechanism in an organic system.

Clearly the polymer of the present invention solves the problems of the prior art. However, as well as

having a T_c greater than or equal to room temperature, the polymer is soluble and is easily processed. For example, it is relatively easy to cast films of the polymer and spin fibres from it. The polymer of the present invention may be used as a ferromagnetic material in typical ferromagnetic applications such as low weight permanent magnets, organic motors and dynamos and magnetic shielding. It is particularly suitable for use as thin film magneto-optic data storage, magnetic security tags, magnetic shielding, magnetic sensors, magnetic transistors and signal processors.

Indeed, further aspects of the invention include thin film magneto-optic data storage comprising a substituted copolymer or ferromagnetic material of the invention; a magnetic security tag comprising a substituted copolymer or ferromagnetic material of the invention; magnetic shielding comprising a substituted copolymer or ferromagnetic material of the invention; a magnetic sensor comprising a substituted copolymer or ferromagnetic material of the invention; a magnetic transistor comprising a substituted copolymer or ferromagnetic material of the invention; and a signal processor comprising a substituted copolymer or ferromagnetic material of the invention.

The invention is exemplified with reference to the following non-limiting description and the accompanying figures in which:

Figure 1 shows the chemical structures of TCNQ and the emeraldine base form of polyaniline along with a suggested structure of the ferromagnetic polymer (PANiCNQ) formed by substituting the emeraldine base form of polyaniline with TCNQ.

Figure 2 shows the optical (UV) spectra of as synthesised PANiCNQ.

Figure 3 shows the saturation magnetisation curve for PANiCNQ measured at room temperature. The inset depicts the temperature dependence of the magnetisation between 77 and 300K.

Figure 4a-d shows alternant images of PANiCQ obtained using an AFM and MFM microscope. Left-hand images are AFM images and right hand images are MFM images.

Figure 4a shows the initial image of a sample from 3b_2, showing the AFM image on the left and the MFM on the right. The MFM is in phase mode.
Figure 4b shows that although the AFM image on the left did not change from that of Figure 4a, in the, a striation is seen moving across the MFM image from right to left.

Figure 4c, shows the striation can again be clearly seen moving across the image in the MFM mode.
Figure 4d shows that the MFM image changed again, indicating the presence of a magnetic domain.

Figure 5 shows the calculated moment from the contaminants of pure Pani and the actual measured moment of 13 samples.

Figure 6 illustrates low Field ESR data for sample 3b_2 showing insulating behaviour.

Example 1

Preparation of polymer

The emeraldine base form of polyaniline was prepared by the method outlined by A.P. Monkman et al in Low Temperature Synthesis of High Molecular weight Polyaniline, Polymer, 37, 3411-3417 (1996). 0.5 g of it was dissolved in 100 ml of n-methyl-2-pyrollidinone (NMP). 1.1g of TCNQ (Lancaster) was added and the solution was refluxed for approximately 24 hours. The solution was then cooled and filtered through a filter paper. The filtered solution was collected and evaporated to give a dark green/black tar polymer. The dark green/black tar polymer was dried under vacuum at 80 °C. It was found that the resultant black polymer absorbs moisture on standing in air.

Example 2

Characterisation of the polymer using Ultraviolet (UV) Spectroscopy.

0.5g of the emeraldine base form of polyaniline was dissolved in 100 ml of n-methyl-2-pyrollidinone (NMP). 2.3 g of TCNQ was added. This forms a blue

solution and upon refluxing as in Example 1, the solution turned dark red/black and exhibited a strong absorption band at λmax = 492 nm (see the solid line spectrum in Figure 2). The solvent was evaporated off under vacuum and the remaining solid was dried at 60 °C at 0.1 mmHg. This yielded a dark green/black polymer which is also readily soluble in NMP. When dissolved in NMP this polymer gives an intense green solution. The UV absorption spectrum of this green solution indicates that a charge transfer has occurred between the TCNQ and the polyaniline, forming stable radicals on both. The UV absorption spectrum shows new absorption maxima at 625 nm and 661 nm with a weaker band at 492 nm (see dashed line in Figure 2). It would appear that the charge transfer and spin separation occurs in the solid state and does not occur in solution.

Example 3

Characterisation of the polymer using Fourier Transform Infra Red (FTIR) Spectroscopy.

A sample of the polymer (PANiCNQ) produced in Example 1 was analysed using FTIR spectroscopy. The FTIR spectrum of this new polymer shows the development of a broad and strong absorption at 2185 cm^{-1} which is ascribed to TCNQ having covalently bonded to the polymer. It is believed that this bonding takes place at the at the amine sites along the polyaniline backbone and that the TCNQ has become a substituted side group along the conjugated backbone. Once formed, this new polymer is still

soluble in NMP and it is believed that charge transfer between the side groups and the backbone occurs once the solvent is removed. In this post-charge transfer state, strong broad absorption between 2600 cm^{-1} and 3300 cm^{-1} is observed, indicative of positively charged nitrogen sites. Also observed is a strong band at 1283 cm^{-1}. This is highly characteristic of CN stretches associated with semiquinoid structures in protonated polyaniline and is highly suggestive that in PANiCNQ, the quinoid imine sites are partially protonated as quinoid peaks at 1508 cm-1 and 1577 cm^{-1} are still observed. It is believed that this protonation occurs during synthesis as a result of hydrogen cyanide which is given off during the attachment of the TCNQ to the polymer chain. This acid will readily protonate any imine sites. As the polymer is hygroscopic, a small broad moisture peak is also present at 3396 cm^{-1}.

From this infra-red data and previous known reactions between TCNQ and amines a tentative structure for PANiCNQ is given in Figure 1. It is possible for the TCNQ to react at the *meta* or *ortho* sites on the benzene rings along the polyaniline backbone. Further, as the synthesis of this new polymer is not well characterised, it must be assumed that both incomplete TCNQ addition and protonation can take place which will give rise to variable physical properties.

Example 4

Characterisation of the polymer using X-ray Spectroscopy.

A sample of the polymer (PANiCNQ) produced in Example 1 was analysed using X-ray spectroscopy. X-ray analysis of the dark green/black polymer revealed the polymer to be amorphous, as would be pure polyaniline.

Example 5

Magnetisation Measurements

To test if the new polymer had a large number of localised spins, magnetisation measurements were made on solid at room temperature using a Vibrating Sample Magnetometer (VSM) that has a sensitivity of 10^{-7} JT^{-1}. A first batch of PANiCNQ was made according to the procedure of Example 1 except that the first batch did not undergo the reflux step and instead was just heated for 10 minutes. Three further batches were made according to the procedure of Example 1. In the first batch of PANiCNQ a weak signal was detected just above the background diamagnetic response. In the three subsequent batches, the reaction time was increased and more attention was paid to the stoichiometric amounts of TCNQ added to the reaction solution, the amount of TCNQ added was increased from 1 mol to 2 mols. Figure 3 shows the saturation magnetisation curve for a sample of one of the latter batches of PANiCNQ. The sample has a mass magnetisation of 0.003 $JT^{-1}Kg^{-1}$. Larger magnetisation was observed

for this sample than for the first batch sample. The inset in Figure 3 depicts the temperature dependence of the magnetisation between 77 K and 300 K. No change in the saturation magnetisation is observed in the temperature range indicating that T_c must lie above room temperature for this material.

The latter batches also revealed much stronger FTIR bands at 2185 cm^{-1}, and a greater degree of charge transfer as seen in absorption spectra than the first batch polymer. Magnetisation measurements on these latter polymers revealed much larger magnetisation, with magnetisation saturation being easily observed at room temperature. These indicate a correlation between the degree of TCNQ substitution, charge transfer and mass magnetisation.

From Figure 3 it is clear that there is a large ferromagnetic component imposed upon a diamagnetic background. Measurements with different samples from one of the latter batches lead to the conclusion that not all the emeraldine base had reacted to form PANiCNQ, and as polyaniline is diamagnetic this accounts for the background.

The mass magnetisation at room temperature for the sample of Figure 3 is approximately 0.003 $JT^{-1}Kg^{-1}$. For reference Ni has a mass magnetisation of 55.4 $JT^{-1}Kg^{-1}$. From the saturation magnetisation curves it is clear that the new material is ferromagnetic at room temperature. Further simple evidence of this is

the fact that lumps of the polymer can be picked up with a small permanent magnet.

Example 6

Thermal Analysis

A sample of PANiCNQ was prepared in accordance with the procedure of Example 1. The sample observed whilst it was heated at a rate of 1°C/min. The thermal analysis of PANiCNQ indicated that the polymer is stable up to and even beyond 500° C. This is characteristic of the emeraldine form of polyaniline. A possible weak glass transition is seen at 260° C.

Example 7

Impurity analysis

FTIR spectroscopy of the new material was made to determine the degree of magnetic impurity. A sample of PANiCNQ was prepared in accordance with the procedure of Example 1. According to spectroscopy measurements less than 50 ppm of the sample is iron. Therefore calculations were carried out on the assumption that the iron would form in the system as a cluster, and thus have the most effect upon the magnetisation. Even then the maximum magnetic moment calculated was of the order 10^{-10} JT^{-1}. The mass magnetisation equipment used in these experiments has a sensitivity of approximately 10^{-7} JT^{-1}. Thus impurities cannot account for the signal measured in the polymer. In addition to this, the first batch

of polymer which showed a weak ferromagnetic signal was retested a month later. The sample had been left in its test capsule in a sealed glass bottle. The ferromagnetic signal had increased dramatically during this time, indicating clearly that the magnetism emanates from the sample and that the solid state reaction must involve a spin separation step which is rather a slow process.

Example 8

Analysis of Polymer Using AFM and MFM

PANiCQ was prepared as described above and samples analysed using an atomic force microscope (AFM) and a magnetic force microscope (MFM). The images were taken from batch number three. Samples were chosen due to their physical size and smoothness. The experiment was carried out upon a digital instruments AFM/MFM at Florida State University. Images obtained using the microscopes are shown in Figures 4a- 4d, with the left hand images showing AFM images obtained and the right hand images showing MFM images. The images are alternant from AFM to MFM respectively as this is necessary to prove that changes in the MFM image are not structural.

Figure 4a shows the initial image of a sample from 3b_2, showing the AFM image on the left and the MFM on the right. The MFM is in phase mode.

Figure 4b shows that the AFM image on the left did not change from that of Figure 4a. However in the MFM image, a striation is seen moving across the image right to left. The MFM is in phase mode.

In Figure 4c, the striation can again be clearly seen moving across the image in the MFM mode.

Fig 4d shows that the MFM image changed again, indicating the presence of a magnetic domain.

The sample examined in Figure 4 was individually run upon an Alternating Gradient Field Magnetometer (AGFM). The inventors noted what appeared to be weak hysteretic behaviour. The data followed a similar trend to all the other data with weak ferromagnetic behaviour upon a diamagnetic background. Without being limited, the inventors expect the magnetism to be most prevalent at the sample surface due to the requirement that the quinoid ring has to be activated. The polymer may even benefit from crushing as the size of the polymer is not important. The hard magnetic properties may be affected as one possibly will break down the inter-chain exchange

Similar images were obtained using other smaller crystalline regions within the sample (data not shown).

Example 9

Testing of Base Materials For Contamination

The base materials were tested for contamination on the Vibrating Sample Magnetometer (VSM) in order to discount the possibility of dirt in the sample. The absolute measurement was not the moment of the sample but the mass magnetisation when comparing results. However for simplicity's sake Figure 5 shows the moment of the sample and contaminants. Fig 5 shows the measured moment against the calculated moment for all the possible contaminants of Pani (polyaniline).

As shown in Figure 5, the measured moment is an order of magnitude less than the calculated moment. Table 1 shows the contamination levels of the transition metals. The table shows the calculated contamination of the transition metals compared to the actual measured moment of the relevant sample. According to the mass spectroscopy there was no Co in any of the samples.

Table 1

Pure Pani sample	Calculated Ni Contamination From mass spec (J/T)	Calculated Fe Contamination From mass spec (J/T)	Measured Moment (J/T)
1	$3*10^{-8}$	$4*10^{-7}$	$4*10^{-8}$
2	$2*10^{-8}$	$3.27*10^{-7}$	$3.5*10^{-8}$
3	$1.5*10^{-8}$	$1.172*10^{-6}$	$1.5*10^{-8}$
4	$1.1*10^{-8}$	$1.19*10^{-7}$	$3*10^{-8}$
5	$1.5*10^{-8}$	$5.9*10^{-8}$	$1*10^{-8}$
6	$1*10^{-8}$	$1.5*10^{-7}$	$1.3*10^{-8}$
7	$7*10^{-9}$	$1.75*10^{-7}$	$1.2*10^{-8}$
8	$8*10^{-9}$	$6.5*10^{-8}$	$1.1*10^{-8}$
9	$1.*10^{-8}$	$1*10^{-7}$	$4*10^{-9}$
10	$1.3*10^{-8}$	$7.9*10^{-8}$	$6*10^{-9}$
11	$6*10^{-9}$	$4.5*10^{-8}$	$1.7*10^{-8}$
12	$1.5*10^{-8}$	$1.26*10^{-7}$	$2.44*10^{-8}$
13	$1.2*10^{-8}$	$1.47*10^{-7}$	$2.3*10^{-8}$

From the table, it is clear that the Ni is approximately of the right level and, apart from the spurious result, the levels of transition metals are within the experimental errors. Accordingly the inventors believe that the Fe content obtained via mass spectroscopy may be an over estimate due to the fact that ArO has an identical mass to Fe. Hence when examining PANiCNQ, Ni is the only real transition element of interest. It is however once again worth explicitly stating that even if one includes all the contaminants it does not account for all the magnetism seen in this sample.

The other base materials of the sample, TCNQ and NMP, are diamagnetic, and were found to be essentially pure as no contaminants can be seen with the VSM.

Example 10

ESR Measurements of Polymer

Electron Spin Resonance (ESR) measurements were made of samples 3b. The ESR measurements lead to the conclusion that the spins in the system are indeed interacting and the number of spins led us to the conclusion that the system was indeed ferromagnetic. Added to this, the occurrence of only one major peak with no hyperfine interactions indicates that the system is indeed pure and only the polymer is acting to give magnetism.

Figure 6 shows the low field behaviour of sample 3b_2. The intensity is much reduced and we are approaching the noise of the system. However the curve visible is indicative of insulating behaviour. Initially before the NMP has been driven off, PANiCNQ is conducting. The inventors assume there is a conduction pathway via the NMP as the Pani backbone still contains a quinoid ring. Although the observation of the conductivity is only qualitative, it is another piece of evidence showing how the system changes over time after the initial fabrication.

All documents referred to in this specification are herein incorporated by reference. Various modifications and variations to the described embodiments of the inventions will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes of carrying out the invention which are obvious to those skilled in the art are intended to be covered by the present invention.

Claims

1. A substituted conjugated polymer comprising a conjugated polymer which is substituted with an organic electron acceptor.

2. The substituted conjugated polymer according to claim 1 wherein the conjugated polymer comprises aromatic groups.

3. The substituted conjugated polymer according to claim 2, wherein the conjugated polymer comprises heterocyclic aromatic groups containing a nitrogen atom in the ring structure.

4. The substituted conjugated polymer according to any one of the preceding claims wherein the conjugated polymer comprises polyaniline, polypyridine, polypyrrole, polyparaphenylene, polyphenylene-vinylene (PPV), polythiophene or polyfluorene.

5. The substituted conjugated polymer according to any one of the preceding claims wherein the conjugated polymer is polyaniline or is a polymer obtained from substituted aniline monomers.

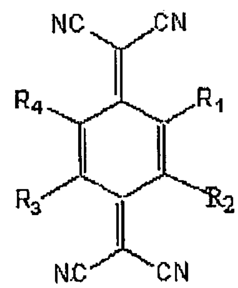
6. The substituted conjugated polymer according to claim 5 wherein the polyaniline is emeraldine base polyaniline.

7. The substituted conjugated polymer according to any one of the preceding claims wherein number average molecular weight of the conjugated polymer is in the range 4000 to 250 000 Dalton.

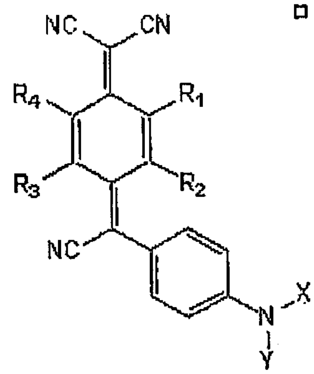
8. The substituted conjugated polymer according to any one of the preceding claims wherein the number average molecular weight of the conjugated polymer is greater than 19000 Dalton.

9. The substituted conjugated polymer according to any one of the preceding claims wherein the electron acceptor comprises tetracyanoquinodimethane (TCNQ), tetracyanonapthoquinodimethane (TNAP), tetracyanoethylene (TCNE), dichlorodicyanobenzoquinone (DDQ), or a TCNQ derivative.

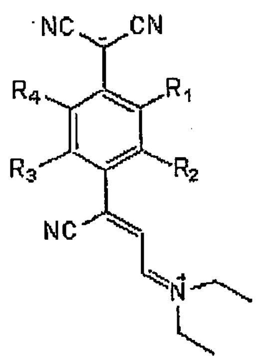
10. The substituted conjugated polymer according to claim 9 wherein the electron acceptor comprises a TCNQ derivative having formula I, formula II,



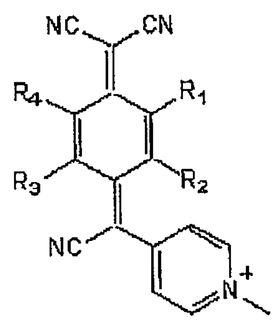
Formula I



Formula II



Formula III



Formula IV

where
$R_1 = R_2 = R_3 = R_4 =$ F, Me, Ph or NCHCHN; or
$R_2 = R_4 =$ H and $R_1 = R_3 =$ I, Br, OMe, CN, $PhCH_2$, a C_1-C_8 alkyl group (preferably hexyl, Me, Et or iPr); or
$R_2 = R_4 =$ H and $R_1 =$ OMe and $R_3 =$ OEt, OiPr, OiButyl, OiPentyl; or
$R_2 = R_4 =$ H and $R_1 =$ OEt and $R_3 =$ SMe; or

$R_2 = R_4 =$ H and R_3 = Me and R_1 = I, Br or Cl; or $R_1 = R_2 = OCH_2CH_2O$ and R_3 = OMe and R_4=H; or $R_2 = R_4$ = H and R_3 = Br and $R_1 = OCH_2CH_2OH$; or $R_2 = R_3 = R_4$ = H and R_1 = Me, Et, OMe, CO_2Me,; and X = Y = C_1-C_8 alkyl group or CH_2CH_2OH; or X = C_1-C_8 alkyl group and Y = CH_2CH_2OH

11. The substituted conjugated polymer according to claim 9 wherein the electron acceptor is tetracyanoquinonedimethane (TCNQ).

12. The substituted conjugated polymer according to any one of the preceding claims wherein the substituted conjugated polymer is polyaniline tricyanoquinonedimethane (PANiCNQ).

13. A ferromagnetic material comprising a substituted conjugated polymer according to any one of the preceding claims.

14. The ferromagnetic material according to claim 13 wherein the ferromagnetic material is the substituted conjugated polymer according to any one of claims 1 to 12.

15. The ferromagnetic material according to claim 13 or claim 14, wherein the material is ferromagnetic at room temperature.

16. The ferromagnetic material according to any one of claims 13 to 15 wherein the material is

ferromagnetic at temperatures above room temperature.

17. The ferromagnetic material according to claim 16 wherein the material is ferromagnetic up to 500 K.

18. The ferromagnetic material according to any one of claims 13 to 17 wherein the material has a mass magnetisation at room temperature of at least 0.003 $JT^{-1}Kg^{-1}$.

19. The ferromagnetic material according to claim 18 wherein the material has a mass magnetisation at room temperature of between 0.003 and 30 $JT^{-1}Kg^{-1}$.

20. A method for producing a ferromagnetic polymer which method comprises reacting a conjugated polymer with an organic electron acceptor.

21. The method according to claim 20, wherein the method comprises the steps:
a) dissolving the conjugated polymer in an appropriate solvent,
b) adding the organic electron acceptor to the solution and refluxing the resultant solution for at least 24 hours,
c) cooling and filtering the refluxed solution from step b and collecting and evaporating the filtrate to form a solid polymer,

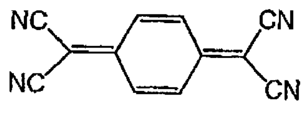
d) drying the polymer from step c, and allowing the polymer to reach a steady ferromagnetic state.

22. The method according to claim 21 wherein the molar ratio of conjugated polymer and organic electron acceptor in the mixture of step b is 1:2.

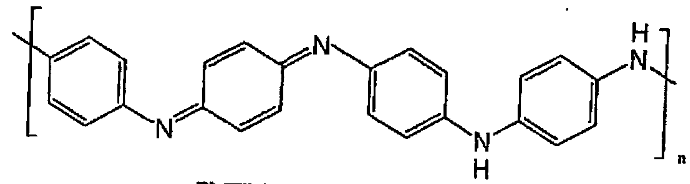
23. The method according to claim 21 or claim 22 wherein the electron acceptor is tetracyanoquinonedimethane (TCNQ).

24. The method according to any one of claims 21 to 23, wherein the conjugated polymer is polyaniline or is a polymer obtained from substituted aniline monomers.

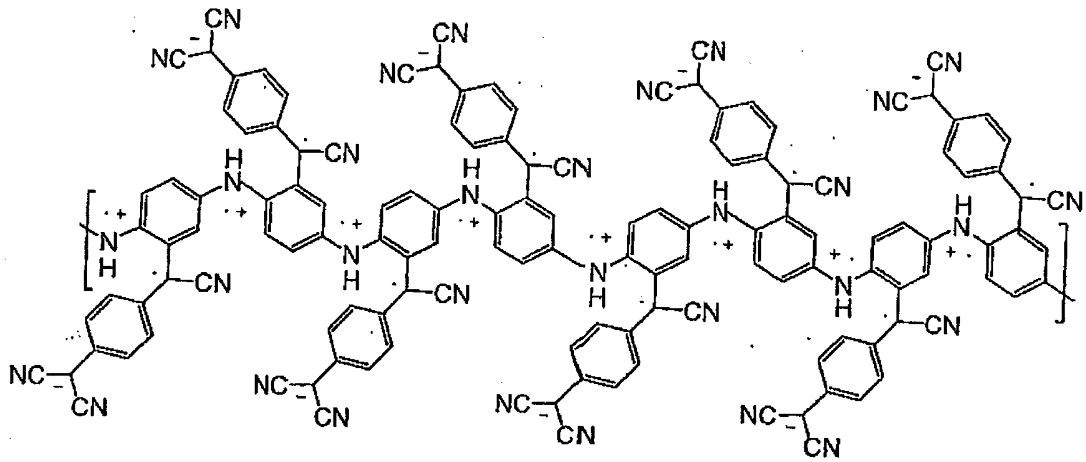
Fig 1



TCNQ



EMERALDINE BASE



PANiCNQ

Fig 2

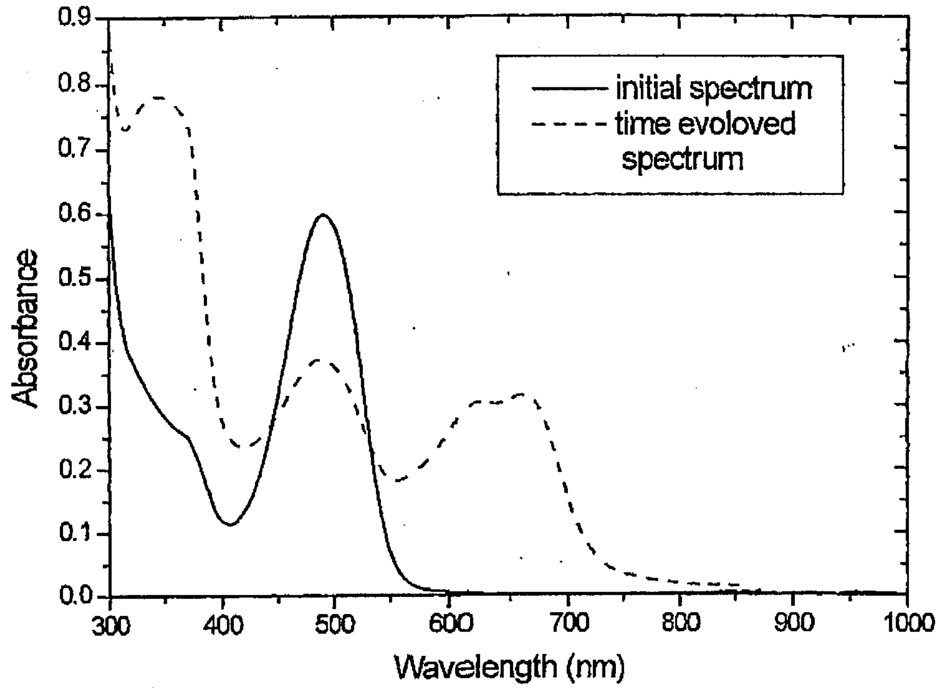

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Absorbance
300
400
500
600
700
800
900
1000
Wavelength (nm)
initial spectrum
time evoloved spectrum

Fig 3

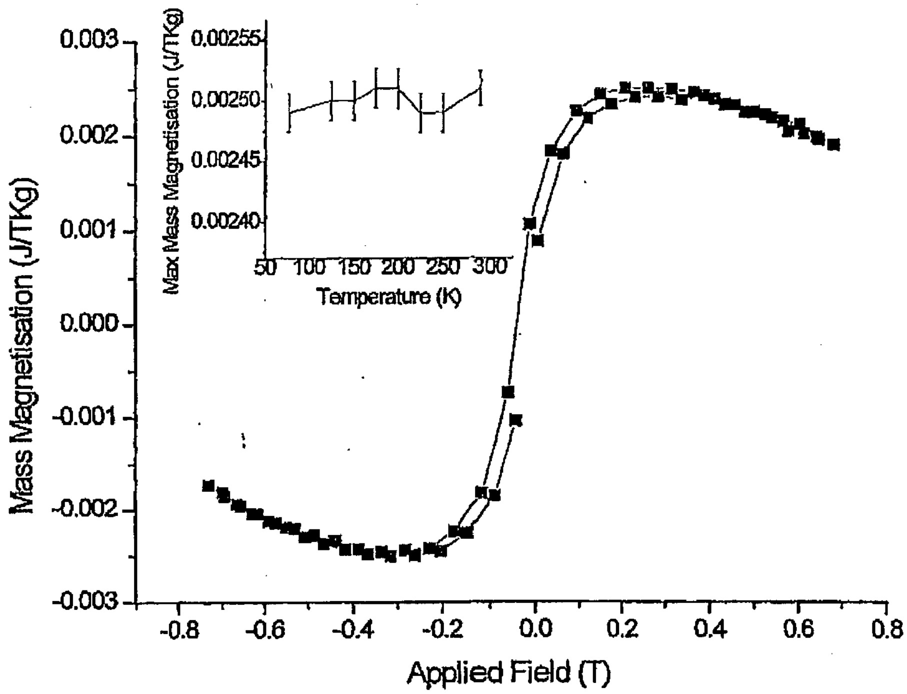

Mass Magnetisation (J/TKg)
0.003
0.002
0.001
0.000
-0.001
-0.002
-0.003
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
Applied Field (T)
Max Mass Magnetisation (J/TKg)
0.00255
0.00250
0.00245
0.00240
50 100 150 200 250 300
Temperature (K)

Figure 4a

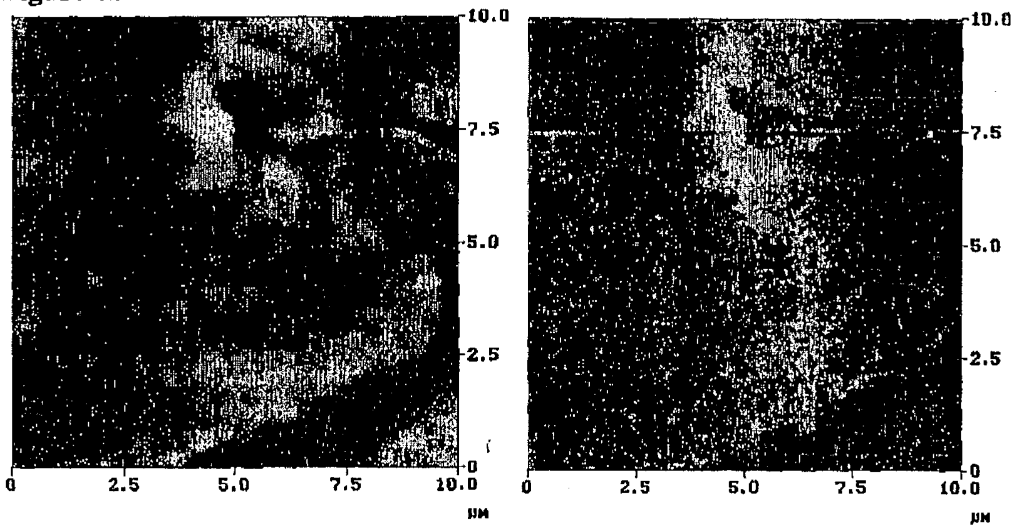


Figure 4b

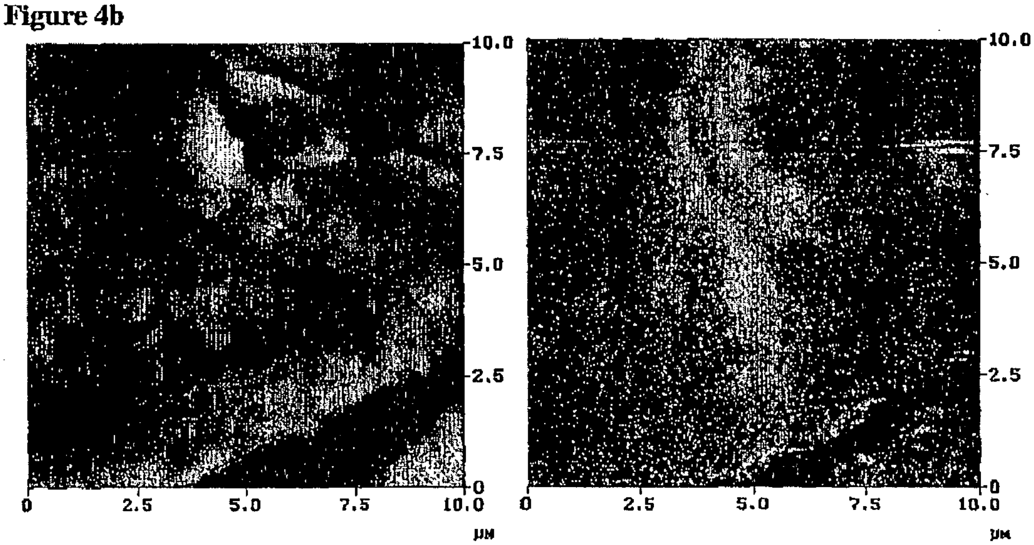


Figure 4c

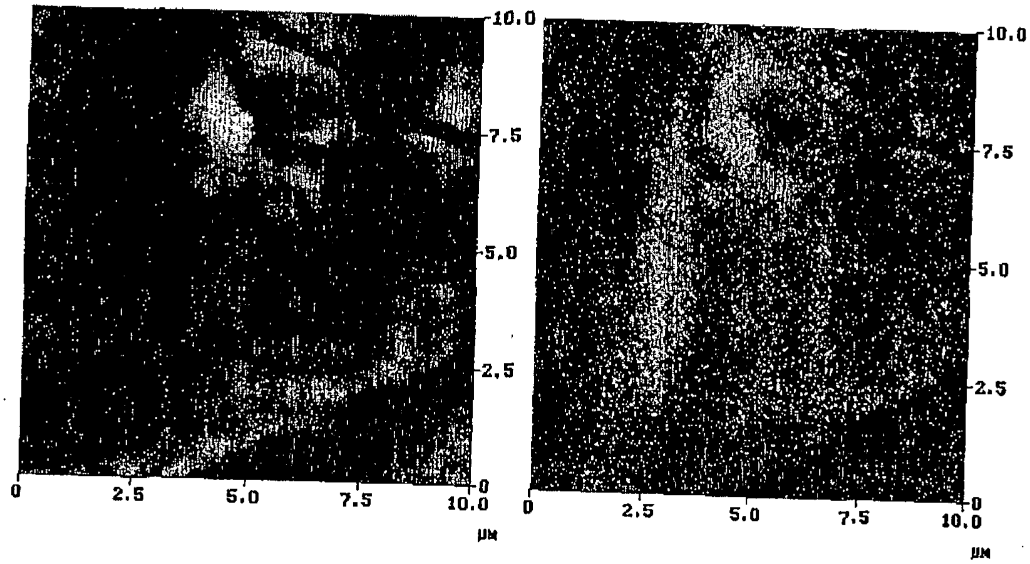


Figure 4d

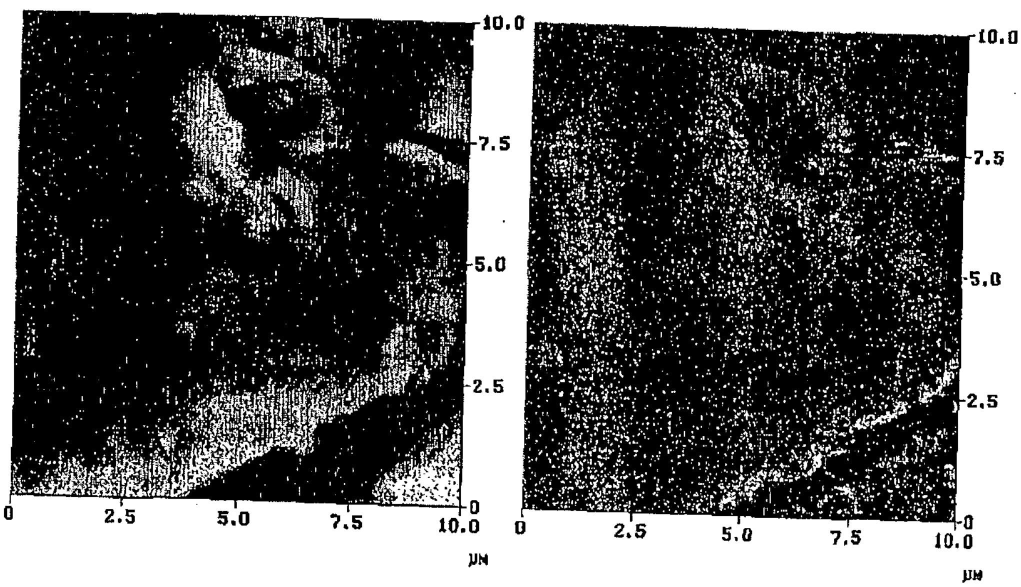
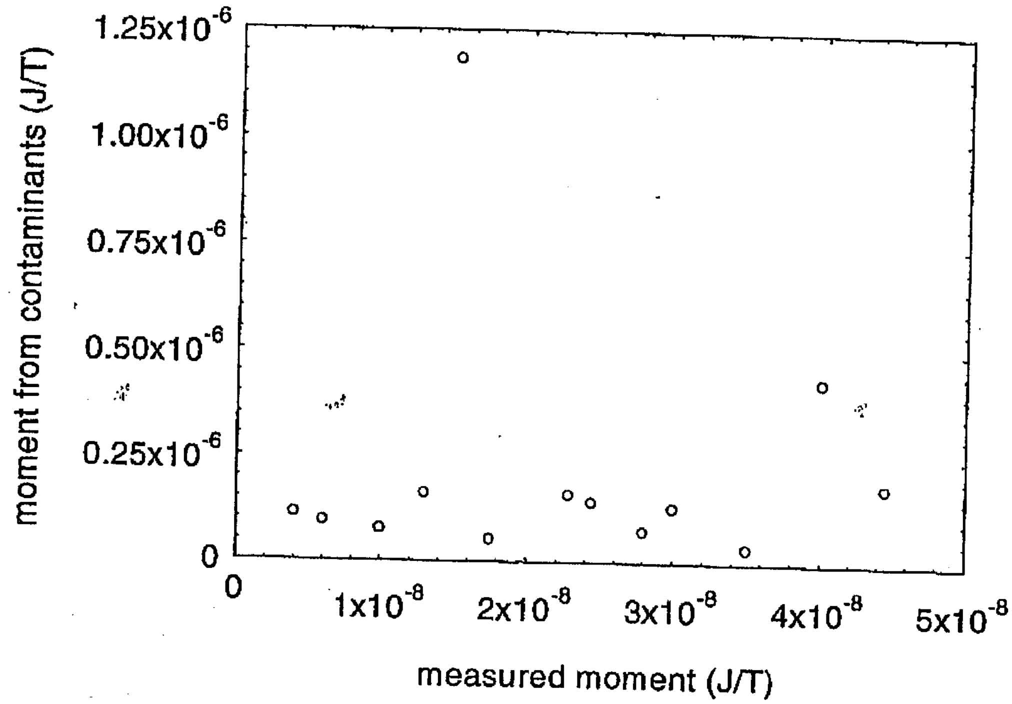
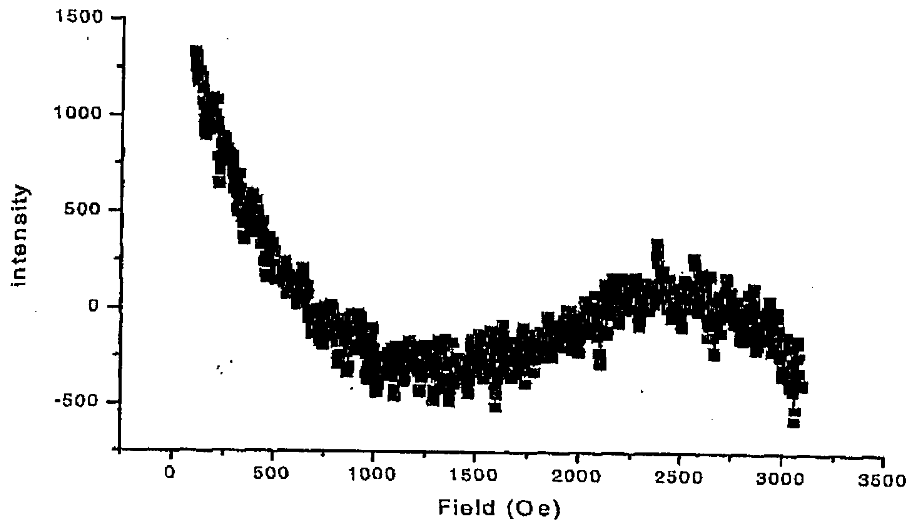


Figure 5



moment from contaminants (J/T)
1.25x10^-6
1.00x10^-6
0.75x10^-6
0.50x10^-6
0.25x10^-6
0
0
1x10^-8
2x10^-8
3x10^-8
4x10^-8
5x10^-8
measured moment (J/T)

Figure 6


1500
1000
500
0
-500
intensity
0
500
1000
1500
2000
2500
3000
3500
Field (Oe)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 03/00254

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G73/02 H01B1/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	DATABASE WPI Week 199348 Derwent Publications Ltd., London, GB; AN 1993-383154 XP002242867 & JP 05 287088 A (NIPPON SODA CO), 2 November 1993 (1993-11-02) abstract	1-4,9-11
A		13-24
X	DATABASE WPI Week 199313 Derwent Publications Ltd., London, GB; AN 1993-105403 XP002242868 & JP 05 047211 A (RICOH KK), 26 February 1993 (1993-02-26)	1-12
A	abstract	13-24

☐ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 May 2003	20/06/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Glanddier, A

INTERNATIONAL SEARCH REPORT

Internatic ilication No
PCT/Gb u3/00254

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
JP 5287088	A	02-11-1993	JP	3334111 B2	15-10-2002
JP 5047211	A	26-02-1993	NONE		